

Ab Initio Characterization of ClNO_2 , *cis*- ClONO , and *trans*- ClONO

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The CCSD(T) method, singles and doubles coupled-cluster theory plus a perturbational estimate of the effects of connected triple excitations, has been used in conjunction with a double polarized triple-zeta (TZ2P) basis set to determine the equilibrium structures, dipole moment, vibrational frequencies, and infrared intensities of ClNO_2 , *cis*- ClONO , and *trans*- ClONO . The *ab initio* results are compared with the available experimental data, and the CCSD(T) results are found to be in excellent agreement with the experimental values, indicating that the CCSD(T) method performs well in describing the weak Cl-N and Cl-O single bonds. The equilibrium structures of *cis*- and *trans*- ClONO are shown to possess normal Cl-O, O-N, and N=O bond distances, in disagreement with a previous study in which the structures were determined based on a normal coordinate analysis using the experimental frequencies. It is shown that incorrect structures were obtained due to a mislabeling of the vibrational modes. A vibrational band previously assigned to an OCINO species is shown to be actually due to *trans*- ClONO . The relative energies of the various species are investigated by computing CCSD(T) energies using atomic natural orbital (ANO) basis sets of spd quality. ClNO_2 is found to be more stable than *cis*- ClONO by 10.7 ± 1.0 kcal/mol while *trans*- ClONO is 3.1 ± 0.8 kcal/mol higher in energy than *cis*- ClONO . The heats of formation of *cis*- ClONO and *trans*- ClONO are predicted (15.4 ± 1.5 and 18.0 ± 1.5 kcal/mol, respectively; 0 K) using isodesmic reactions involving H_2O , HOCl , and *cis*- and *trans*-HONO.

Introduction

Nitrosyl chloride, ClNO_2 , and *cis*- and *trans*-chlorine nitrite, ClONO , are of some interest as minor constituents in stratospheric chemistry.¹ While it is much more likely that ClONO will form in the stratosphere (i.e., from $\text{ClO} + \text{NO}$ and also from $\text{ClNO} + \text{Cl}_2\text{O}$) rather than ClNO_2 , it has been shown² that ClONO readily isomerizes to ClNO_2 . Due to this rapid isomerization the ClNO_2 isomer is much better characterized experimentally. In fact, the molecular structure,³ vibrational spectrum,⁴ and heat of formation⁵ of ClNO_2 are all known experimentally. In contrast, the experimental⁶ heat of formation of ClONO does not distinguish between the *cis* and *trans* isomers, and although the vibrational spectrum^{2,7,8} and pure rotational spectrum⁹ of *cis*- ClONO have been observed, there is some disagreement as to the nature of its molecular structure. Specifically, a normal coordinate analysis based on the observed vibrational spectrum leads to a molecular structure with a very long Cl-O bond distance—suggestive of a weakly bound complex between the Cl and ONO radicals—while analysis of the microwave data leads to a structure with a more normal Cl-O bond distance. However, in the analysis of the microwave experiments some of the molecular parameters were assumed, based on analogy with CH_3ONO , since data from only two isotopomers are not sufficient to determine the five unique geometrical parameters.

Based on analogy with other XONO compounds, it is expected that there will be a *cis* and *trans* form of ClONO . In gas-phase experimental studies^{2,8,9} of ClONO , only the *cis* form has been observed—indicating that the *cis* form is lower in energy (similar¹⁰ to FONO). There are no experimental observations that have been attributed to *trans*- ClONO . In matrix isolation experiments⁷ there is one vibrational band that has been attributed to an OCINO species, but we show that this band is in fact due to *trans*- ClONO . We also explain why this is the only vibrational band of *trans*- ClONO to be observed. Furthermore, after extensive searches of the OCINO region of the potential energy surface, it is concluded that an OCINO isomer does not exist.

The purpose of the present investigation is to characterize fully the ground electronic state of the ClNO_2 , *cis*- ClONO , and *trans*-

ClONO species using state-of-the art *ab initio* quantum mechanical methodology. This includes the accurate determination of the equilibrium structure, dipole moment, vibrational frequencies, and infrared (IR) intensities. In addition, the relative energetics and the heat of formation of the ClNO_2 and ClONO species are accurately determined. The present study explains the experimentally observed data for *cis*- ClONO and resolves the disagreement concerning its molecular structure. It is also of interest to contrast and compare the present results with those published previously¹⁰ for *cis*- and *trans*-FONO because there is still some debate as to the molecular structure of *cis*-FONO.

In three previous *ab initio* studies of ClNO_2 and/or ClONO , calculations were performed at low levels of theory with small one-particle basis sets.^{11,12} It is well-known that the electronic structure of molecules composed of several electronegative atoms bonded together is often not described even qualitatively correctly at low levels of theory. Thus these past studies were not of sufficient accuracy to resolve the question of the molecular structure of *cis*- ClONO , nor were they of sufficient accuracy to determine reliably the relative energetics and heats of formation of *cis*- ClONO and *trans*- ClONO . The *ab initio* methods used in the present investigation are described in the next section. The following section contains results and discussion, and conclusions are summarized in the final section.

Computational Methods

Equilibrium geometries were determined with a TZ2P basis set at the CCSD(T) level of theory¹³ (singles and doubles coupled-cluster theory plus a perturbational estimate of the effects of connected triple excitations). The TZ2P basis set consists of Dunning's¹⁴ [5s3p/3s] contraction of Huzinaga's¹⁵ (10s6p/5s) primitive Gaussian functions for O and H, respectively, augmented with two sets of polarization functions¹⁶ ($\alpha_4 = 2.314, 0.645$ for O; $\alpha_p = 1.407, 0.388$ for H). The Cl TZ2P basis set is composed of McLean and Chandler's¹⁷ [6s5p] contracted functions supplemented with two sets of polarization functions ($\alpha_4 = 1.072, 0.357$). For the TZ2P basis set, all six Cartesian components of the d functions were included in the basis set. Coupled-cluster analytical gradient methods^{18,19} were used to locate the equilibrium structure. Quadratic force constants, harmonic frequencies, and

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TABLE 1: Total Energies (hartrees), Equilibrium Structure, Rotational Constants (MHz), Dipole Moment (D), and Harmonic Frequencies (cm⁻¹) of ClNO₂ Obtained at the CCSD(T)/TZ2P Level of Theory^a

	theory	expt ^b
<i>E</i>	0.428576	—
μ	0.45	0.42
<i>T</i> ₁ ^c	0.022	—
<i>r</i> _{CIN}	1.877	1.840
<i>r</i> _{NO}	1.198	1.202
\angle ONO	132.0	130.6
<i>A</i> _e	13190	13240
<i>B</i> _e	5063	5174
<i>C</i> _e	3659	3721
$\omega_1(a_1)$; N—O s-str	1290 (334)	1286 vs
$\omega_2(a_1)$; ONO bend	805 (215)	793 vs
$\omega_3(a_1)$; Cl—N str	371 (55)	370 vs
$\omega_4(b_1)$; N—O a-str	1688 (371)	1685 vs
$\omega_5(b_1)$; ClNO a-bend	409 (0.4)	408 vw
$\omega_6(b_2)$; op-bend	658 (4.8)	652 m

^a The energy is reported as $-(E + 664)$. Bond lengths in Å and angles in degrees. IR absorption intensities (in parentheses) in km/mol, op = out-of-plane. ^b Vibrationally averaged dipole moment, structure and rotational constants from ref 3; fundamental frequencies from ref 4; vs = very strong; vw = very weak; m = moderate. ^c See ref 27 for a description of the *T*₁ diagnostic.

IR intensities were determined by finite differences of analytical gradients. The dipole moment was determined as the derivative of the energy with respect to an external electric field.

In order to determine accurate relative energies and heats of formation, two isodesmic reactions have been used (these will be given later). The reaction energies have been evaluated at the MP2 (second-order Møller–Plesset perturbation theory), CCSD and CCSD(T) levels of theory using atomic natural orbital (ANO) basis sets.²⁰ The H and O ANO basis sets are those of Almlöf and Taylor,²⁰ while the Cl ANO basis set is taken from Bauschlicher and Roos.²¹ For Cl, the density matrices of the neutral atom and the negative ion were averaged. The primitive basis sets are van Duijneveldt's²² (13s8p/8s) sets augmented with an even tempered sequence of (6d4f2g/6p4d3f) polarization functions for O and H, respectively. The polarization function orbital exponents are obtained from $\alpha = 2.5^n \alpha_0$, $n = 0 \dots k$, with $\alpha_0 = 0.13, 0.39$, and 1.24 for the O d, f, and g functions, respectively; $\alpha_0 = 0.10, 0.26$, and 0.40 for the H p, d and f functions. The Cl primitive basis set is Partridge's²³ (19s14p) set augmented with a (6d4f2g) set of polarization functions with $\alpha_0 = 0.06, 0.19$, and 0.56 for the Cl d, f and g functions. The basis set denoted ANO1 consists of 5s4p2d, 4s3p2d, and 4s2p ANOs on Cl, O, and H, respectively, while the ANO2 basis set is composed of 5s4p2d1f, 4s3p2d1f, and 4s2p1d ANOs on Cl, O, and H. The ANO3 set consists of 6s5p3d2f, 5s4p3d2f, and 4s3p2d ANOs on Cl, O, and H, respectively, while the ANO4 basis is composed of 6s5p3d2f1g, 5s4p3d2f1g, and 4s3p2d1f ANOs on Cl, O, and H. For the ANO basis sets, only the spherical harmonic components of the d, f and g-type functions were included.

The coupled-cluster geometry optimizations were performed with the TITAN²⁴ program system. The MP2 and coupled-cluster single-point energies were performed with the TITAN coupled-cluster programs interfaced to the SEWARD²⁵ integral program and the SWEDEN²⁶ self-consistent field and integral transformation programs.

Results and Discussion

A. Equilibrium Structures and Vibrational Frequencies. The CCSD(T)/TZ2P equilibrium structure, dipole moment, harmonic frequencies, and IR intensities of ClNO₂ are presented in Table 1 together with the relevant experimental data. Note that the experimental structure, rotational constants, and dipole moment³ are vibrationally averaged quantities, and the experimental vibrational frequencies⁴ refer to fundamentals. The *T*₁ diag-

TABLE 2: Total Energies (hartrees), Equilibrium Structures, Rotational Constants (MHz), Dipole Moments (D), and Harmonic Frequencies (cm⁻¹) of *cis*- and *trans*-ClONO Obtained at the CCSD(T)/TZ2P Level of Theory^a

	<i>cis</i> -ClONO		<i>trans</i> -ClONO	
	theory	expt ^b	theory	expt ^c
<i>E</i>	0.409540	—	0.404976	
μ	0.62		0.76	
<i>T</i> ₁ ^d	0.025		0.023	
<i>r</i> _{ClO}	1.720	1.732	1.713	
<i>r</i> _{ON}	1.489		1.542	
<i>r</i> _{NO}	1.161		1.156	
\angle ONO	115.6		108.1	
\angle ClON	113.6	115.7	107.5	
<i>A</i> _e	17902	18230	49579	
<i>B</i> _e	4458	4572	2988	
<i>C</i> _e	3569	3650	2818	
$\omega_1(a')$; N=O str	1715 (252)	1715	1754 (297)	1752
$\omega_2(a')$; ONO bend	850 (17)	858	855 (102)	
$\omega_3(a')$; Cl—O str	638 (21)	644	662 (182)	
$\omega_4(a')$; O—N str	416 (167)	406	407 (98)	
$\omega_5(a')$; ClON bend	249 (0.1)	260–280	262 (0.2)	
$\omega_6(a'')$; torsion	341 (1.3)	344	170 (0.01)	

^a The energy is reported as $-(E + 664)$. Bond lengths in Å and angles in degrees. IR absorption intensities (in parentheses) in km/mol. ^b Vibrationally averaged structure and rotational constants taken from ref 9; gas-phase fundamental frequencies from ref 2; note also the matrix isolation experiments discussed in ref 7. ^c Fundamental from ref 7; note that this vibrational band was previously assigned to an OCINO species—see text. ^d See ref 27 for a description of the *T*₁ diagnostic.

nistic²⁷ for ClNO₂ suggests that the CCSD(T)/TZ2P level of theory should perform very well for ClNO₂, and the excellent agreement between theory and experiment supports this assertion. The largest deviation for a rotational constant is only 111 MHz, and the experimental and *ab initio* dipole moments agree to within 0.03 D. There is also excellent agreement between the *ab initio* harmonic frequencies and the experimental fundamentals. Since the anharmonic correction for most of the vibrations should be less than 15 cm⁻¹ (only ν_4 is likely to have an anharmonic correction that is slightly larger), it is apparent that this agreement is not due to a fortuitous cancellation of errors. Finally, it is of interest to note that the experimental descriptions of the strength of the IR absorptions are also in qualitative agreement with the *ab initio* IR intensities. On the basis of this excellent agreement, there is reason to expect that the CCSD(T)/TZ2P level of theory will also perform well for *cis*- and *trans*-ClONO.

Table 2 contains the CCSD(T)/TZ2P predictions for *cis*- and *trans*-ClONO together with the available experimental data (again, the rotational constants⁹ are vibrationally averaged and the vibrational frequencies² refer to fundamentals). While the *T*₁ diagnostic value is somewhat larger for *cis*- and *trans*-ClONO than that found for ClNO₂, it is still within the range where the CCSD(T)/TZ2P level of theory should perform well. Comparison of the experimentally observed quantities with the *ab initio* values for *cis*-ClONO shows that again there is excellent agreement between theory and experiment. In this case the largest deviation for a rotational constant is only 328 MHz, while the largest difference for a vibrational frequency is ≈ 11 cm⁻¹. Again, since most of the vibrations will have anharmonic corrections smaller than 15 cm⁻¹, this agreement is not due to a cancellation of errors.

Also included in Table 2 are the two geometrical parameters estimated by Kawashima *et al.*⁹ These are in good agreement with the CCSD(T)/TZ2P values with part of the remaining difference attributable to the assumptions made by Kawashima *et al.* However, the *ab initio* structure is not in good agreement with the geometry deduced by Janowski *et al.*² In particular they obtained a Cl—O bond distance of 1.9 Å based on a normal coordinate analysis procedure. This apparent discrepancy is due to mislabeling of the vibrational modes. The vibrational mode

descriptions given in Table 2 were determined by potential energy distribution analyses of the CCSD(T)/TZ2P Hessian matrices. While there is inevitably some mixing between different modes, in this case the mixing between the various internal degrees of freedom is not that substantial. Mislabeling of the vibrations in *cis*-ClONO was also a feature of the matrix isolation experiments of Tevault and Smardzewski.⁷ It is therefore not surprising that Janowski *et al.* obtained an inaccurate molecular structure for ClONO since the appropriate vibrational mode labels for XONO type molecules were not known at that time.

Note that Kawashima *et al.* also estimated dipole moment components for *cis*- and *trans*-ClONO on the basis of some assumed bond dipole values. These are in error, indicating that the assumed bond dipole values are not correct. The *ab initio* dipole moment values presented in Table 2 should be considerably more accurate.

Tevault and Smardzewski⁷ also observed a vibrational band at 1752 cm⁻¹ that they attributed to an OCINO species. The OCINO region of the potential energy surface has been extensively examined at the CCSD(T)/TZ2P level of theory, and no such isomer was found. In addition, examination of the CCSD(T)/TZ2P frequencies for *trans*-ClONO suggests strongly that this band should be assigned to *trans*-ClONO. For both HONO and FONO (e.g., see refs 10 and 19), the *trans* isomer possesses an N=O stretch frequency that is larger than the *cis* form, although the magnitude of this difference varies. Nevertheless, the CCSD(T)/TZ2P prediction of the N=O stretch in *trans*-ClONO is in excellent agreement with the band observed by Tevault and Smardzewski, and furthermore the *ab initio* IR intensities show why this particular band was the only one observed for *trans*-ClONO. That is, the concentration of *trans*-ClONO is much lower than that of *cis*-ClONO (due to the thermodynamic stability of the *cis* structure relative to the *trans* structure), and the N=O stretch has by far the largest IR intensity. Thus, the CCSD(T)/TZ2P calculations for *cis*- and *trans*-ClONO reported herein are consistent with all experimentally observed quantities and are able to explain some problems in the interpretation of these experiments.

It is of interest to compare the current results for *cis*-ClONO to those published previously¹⁰ for *cis*-FONO because there remains some debate as to the molecular structure of *cis*-FONO (e.g., see refs 10 and 28 and references therein). In ref 10 it was concluded that *cis*-FONO adopted a molecular structure with "normal" bond distances. That is, the F-O, O-N, and N=O bond distances are all in the range that would be considered "conventional" single and double bonds. Conversely, it has also been asserted,²⁸ on the basis of calculations employing density functional theory (DFT), that the F-O bond distance is very long, similar to that found in the FOOF or FON molecules. The fact that *cis*-ClONO possesses normal bond distances would tend to suggest that *cis*-FONO may as well. However, this type of analogy cannot be taken too far since the behavior of FOOF and ClOOC (see ref 29) is quite different. In fact, there are no known closed-shell molecules that exhibit an abnormally long Cl-O bond distance. (ClON might be a candidate, although we are not aware of any experimental reports suggesting the existence of ClON; however, a ClON minimum with a long Cl-O bond is obtained at the CCSD(T)/TZ2P level of theory.) It may be stated with certainty, however, that the mode descriptions for the experimentally observed vibrational bands of *cis*-FONO that were assigned based on theoretical calculations¹⁰ are entirely consistent with those reported here for *cis*-ClONO. Moreover, given the excellent agreement between CCSD(T) and experiment for *cis*-ClONO, it would be interesting to know how DFT performs for *cis*-ClONO since DFT and CCSD(T) do not agree^{10,28} for *cis*-FONO. A more detailed *ab initio* investigation of *cis*-FONO is in progress and will be reported in due course.

Since the CCSD(T)/TZ2P quadratic force constants for

TABLE 3: Quadratic Force Constants of ClNO₂, *cis*-ClONO, and *trans*-ClONO Obtained at the CCSD(T)/TZ2P Level of Theory^a

	ClNO ₂	<i>cis</i> -ClONO	<i>trans</i> -ClONO
F_{11}	1.639	2.975	3.323
F_{21}	0.914	0.617	0.241
F_{22}	12.259	1.516	1.562
F_{31}	-0.579	0.029	-0.029
F_{32}	0.756	1.910	1.860
F_{33}	2.048	13.513	13.846
F_{41}	-	0.199	0.306
F_{42}	-	0.514	0.178
F_{43}	-	-0.073	0.181
F_{44}	9.389	1.426	1.005
F_{51}	-	-0.310	0.253
F_{52}	-	0.549	0.179
F_{53}	-	0.571	0.504
F_{54}	0.442	-0.043	0.373
F_{55}	1.017	2.178	1.889
F_{66}	0.413	0.201	0.117

^a Units are aJ/Å², aJ/Å·rad, and aJ/rad². See text for definition of the symmetry internal coordinates (aJ = attoJoules).

ClNO₂, *cis*-ClONO, and *trans*-ClONO should be quite accurate, they are presented in Table 3 to aid in the interpretation of future experimental studies. Symmetry internal coordinates have been used for ClNO₂, and these are defined as

$$S_1(a_1) = r_{\text{ClN}} \quad (1.1)$$

$$S_2(a_1) = \frac{1}{\sqrt{2}}(r_{\text{NO}_1} + r_{\text{NO}_2}) \quad (1.2)$$

$$S_3(a_1) = \angle \text{ONO} \quad (1.3)$$

$$S_4(b_1) = \frac{1}{\sqrt{2}}(r_{\text{NO}_1} - r_{\text{NO}_2}) \quad (1.4)$$

$$S_5(b_1) = \frac{1}{\sqrt{2}}(\angle \text{ClNO}_1 - \angle \text{ClNO}_2) \quad (1.5)$$

$$S_6(b_2) = \delta \quad (1.6)$$

where δ refers to the Cl-NO₂ out-of-plane bend coordinate. For ClONO, the following internal coordinates have been used:

$$S_1(a') = r_{\text{ClO}} \quad (1.7)$$

$$S_2(a') = r_{\text{ON}} \quad (1.8)$$

$$S_3(a') = r_{\text{NO}} \quad (1.9)$$

$$S_4(a') = \angle \text{ClON} \quad (1.10)$$

$$S_5(a') = \angle \text{ONO} \quad (1.11)$$

$$S_6(a'') = \tau \quad (1.12)$$

where τ refers to the ClONO torsional coordinate.

B. Relative Energies and Heats of Formation. Experience has shown that it is necessary to use large one-particle basis sets in order to compute reliably the energy difference between the XNO₂ and XONO compounds. This is due to the different bonding situations, and therefore large ANO basis sets, described earlier, have been used for this purpose. The energy differences between ClNO₂ and *cis*- and *trans*-ClONO, computed at different levels of theory with four different ANO basis sets, are given in Table 4. The positive values indicate that ClNO₂ is more stable than *cis*- and *trans*-ClONO. Examination of the MP2 and coupled-

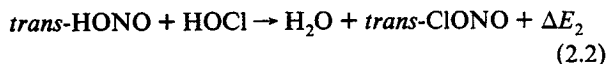
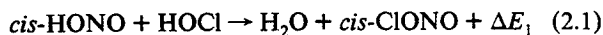
TABLE 4: Energies (kcal/mol) of *cis*-ClONO and *trans*-ClONO Relative to ClNO₂. CCSD(T)/TZ2P Geometries Were Used^a

	<i>cis</i> -ClONO	<i>trans</i> -ClONO
MP2/ANO1	18.1	21.1
MP2/ANO2	18.4	21.7
MP2/ANO3	18.3	21.5
MP2/ANO4	18.4	21.7
CCSD/ANO1	9.9	12.3
CCSD/ANO2	10.4	13.1
CCSD/ANO3	10.4	13.1
CCSD/ANO4	10.7	13.5
CCSD(T)/TZ2P	11.9	14.8
CCSD(T)/ANO1	11.4	14.3
CCSD(T)/ANO2	11.9	15.0
CCSD(T)/ANO3	11.8	15.0
CCSD(T)/ANO4	12.1	15.4
ΔZPVE	-1.4	-1.6

^a Zero-point vibrational energies not included in the electronic energy differences—see text for energy differences where these are included. The ΔZPVE quantities were determined using CCSD(T)/TZ2P harmonic frequencies.

cluster results shows that second-order perturbation theory does not yield a good estimate of the correlation energy contribution to these energy differences. However, comparison of the CCSD and CCSD(T) results shows that the correlation energy contribution is relatively stable once an iterative technique is used. In addition, comparison of the CCSD(T)/ANO2 and CCSD(T)/ANO4 sets of energy differences shows good convergence with respect to the one-particle basis set. Taking the CCSD(T)/ANO4 results as the best estimate of the electronic contribution and correcting for the effects of zero-point vibrational energies (ZPVE, determined using the CCSD(T)/TZ2P harmonic frequencies), our best estimate is that *cis*-ClONO is less stable than ClNO₂ by 10.7 kcal/mol and *trans*-ClONO is further destabilized by 3.1 kcal/mol (both at 0 K). The ClNO₂-*cis*-ClONO energy difference is conservatively estimated to be accurate to within ±1.0 kcal/mol, while the *trans*-*cis* energy difference is estimated to be accurate to better than ±0.8 kcal/mol. Interestingly, the *trans*-*cis* energy difference is similar to that predicted¹⁰ for *cis*- and *trans*-FONO.

For evaluating the importance of *cis*- and *trans*-ClONO in atmospheric chemistry, it is of interest to determine accurate heats of formation. Currently, the accepted experimental value⁶ for the heat of formation of ClONO (no distinction made for *cis* or *trans*) is 13.4 kcal/mol at 298 K. One approach to determine an accurate *ab initio* heat of formation is to construct an isodesmic reaction containing the molecule of interest, for which the experimental heats of formation of all the other species are known to high accuracy. For *cis*- and *trans*-ClONO, the following isodesmic reactions have been used:



The electronic energies for reactions 2.1 and 2.2, ΔE₁ and ΔE₂, respectively, have been evaluated at the MP2, CCSD, and CCSD(T) levels of theory using the large ANO1 through ANO4 basis sets. CCSD(T)/TZ2P equilibrium geometries have been used (the CCSD(T) geometries of H₂O, HOCl, and *cis*- and *trans*-HONO have been taken from previous^{19,29} work). The results are summarized in Table 5. ΔE₁ and ΔE₂ exhibit a larger dependence on the treatment of electron correlation than is typical for isodesmic reactions. However, the difference between the CCSD and CCSD(T) values is fairly small, indicating that the CCSD(T) results are nearly converged with respect to the

TABLE 5: Energies (kcal/mol) of Reactions (2.1 and 2.2). CCSD(T)/TZ2P Geometries Were Used^a

	ΔE ₁	ΔE ₂
MP2/ANO1	-9.1	-5.6
MP2/ANO2	-8.4	-5.1
MP2/ANO3	-9.0	-5.5
MP2/ANO4	-8.8	-5.3
CCSD/ANO1	-4.7	-2.0
CCSD/ANO2	-4.0	-1.3
CCSD/ANO3	-4.4	-1.6
CCSD/ANO4	-4.2	-1.4
CCSD(T)/TZ2P	-7.2	-3.7
CCSD(T)/ANO1	-7.1	-3.8
CCSD(T)/ANO2	-6.3	-3.1
CCSD(T)/ANO3	-6.9	-3.4
CCSD(T)/ANO4	-6.6	-3.2
ΔZPVE	-1.2	-1.4

^a Zero-point vibrational energies not included in the electronic energy differences—see text for energy differences where these are included. The ΔZPVE quantities were determined using CCSD(T)/TZ2P harmonic frequencies.

treatment of electron correlation. Examination of the results in Table 5 further shows that the difference between the ANO2 and ANO4 results is consistently small, and therefore ΔE₁ and ΔE₂ are also close to being converged with respect to improvements in the one-particle basis set. Taking the CCSD(T)/ANO4 quantities as best estimates, and correcting these for ZPVE, gives ΔE₁ and ΔE₂ values of -7.8 and -4.6 kcal/mol. These values are estimated to be accurate to within ±1.0 kcal/mol. Using these best estimates together with the experimental⁵ heats of formation for H₂O, HOCl, and *cis*- and *trans*-HONO, the heats of formation of *cis*- and *trans*-ClONO are determined to be 15.4 and 18.0 kcal/mol (0 K). These values are expected to be accurate to better than ±1.5 kcal/mol (the uncertainty in the experimental heat of formation of HOCl adds an additional 0.5 kcal/mol). Note that these heats of formation suggest that the *trans*-*cis* energy difference is 2.6 kcal/mol rather than the 3.1 kcal/mol determined by direct calculation. This difference arises due to the difference¹⁹ in the *ab initio* and experimental *cis*-*trans* energy separation in HONO. However, the small difference is well within the estimated uncertainties, and we note that our best estimate for the *trans*-*cis* energy difference in ClONO is 3.1 ± 0.8 kcal/mol.

Correcting the computed heat of formation of *cis*-ClONO for temperature effects to 298 K yields a value of 14.5 ± 1.5 kcal/mol, which is in good agreement with the experimental⁶ value of 13.4 kcal/mol. A further test of the reliability of the present *ab initio* energetics is given by combining the computed *cis*- and *trans*-ClONO heats of formation (0 K) with the computed ClNO₂ energy differences to obtain the heat of formation of ClNO₂. Performing this, we obtain 4.7 kcal/mol (from *cis*-ClONO) and 4.2 kcal/mol (from *trans*-ClONO), which both compare very favorably with the experimental⁵ heat of formation of ClNO₂ (4.2 ± 0.4 kcal/mol at 0 K).

Conclusions

The CCSD(T)/TZ2P level of theory has been used to determine the equilibrium structures, dipole moments, vibrational spectrum, and IR intensities of ClNO₂, *cis*-ClONO, and *trans*-ClONO. The *ab initio* results for ClNO₂ and *cis*-ClONO agree very well with the experimentally observed quantities. A potential energy distribution analysis of the *cis*-ClONO CCSD(T)/TZ2P Hessian shows that in an earlier normal coordinate analysis² the labeling of the normal vibrations was incorrect, leading to a flawed molecular structure. Thus the *ab initio* results presented herein have resolved the difference between the *cis*-ClONO molecular structures determined in two separate experiments. It has also been shown that a vibrational band observed in matrix isolation

experiments⁷ and attributed to an OCINO species is in fact due to *trans*-ClONO. On the basis of an extensive search of the OCINO region of the ground-state potential energy surface, it is asserted that an OCINO species does not exist. Finally, CCSD-(T) calculations using large ANO basis sets have been performed to determine accurate heats of formation of *cis*- and *trans*-ClONO (15.4 ± 1.5 and 18.0 ± 1.5 kcal/mol, respectively; 0 K) and also to determine that *cis*-ClONO is higher in energy than ClNO₂ by 10.7 ± 1.0 kcal/mol and that *trans*-ClONO is an additional 3.1 ± 0.8 kcal/mol higher in energy.

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